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ACTIVATION OF WASTE TYRES CHAR UPON CYCLIC OXYGEN CHEMISORPTION-DESORPTION

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ABSTRACT

Activation of waste tyres char upon cyclic oxygen chemisorption-desorption permits a controlled development of porosity versus burn-off using air as fed gas for the activation process. A slow but monotonical increase of BET surface area is obtained from cycle to cycle. Initial lead to the development of mesoporosity without generating micropores and then the micropore volume is increased whereas a decrease of narrow mesopore (20-80 nm) volume is observed, probably as a consequence of mesopore widening. Although the S_{BET} reaches relatively low values (below 250 m²/g) even after 15 cycles, this surface development is associated with low burn-off values (around 22% for indicated BET surface area) and corresponds in an important percentage (up to about 50%) to external (non-micropore) area. Temperatures around 210 and 550 °C for chemisorption and desorption, respectively, have been found as optimum for the purpose of preparing granular mesoporous carbons which can be interesting candidates as catalytic supports for liquid phase applications.

INTRODUCTION

Waste tyres represent an important environmental problem nowadays due to the high generation, more than 5 million of tons per year in Europe, USA and Japan, and potential polluting power¹. In addition to physical recycling by retreading, as additive in asphalt formulation or other applications, several thermal methods based on pyrolysis and/or gasification of waste tyre rubber have been studied.

The typical composition of pyrolysis products is 0-30 % gases, 20-55% oil and 30-40% char^{2,3}. The chemical composition of oil and gas fractions has been extensively studied to recover valuable chemicals as aromatics, or to be used as fuel due to their high heating power: about 35 MJ/Nm³ and 40 MJ/kg for gas and oil fraction, respectively^{2,4}. Important attention has also been paid to the valorization of char. The chars from waste tyres pyrolysis usually do not have adequate characteristics to be used directly in commercial applications. For this reason several methods have been studied to modify the properties of these chars to be applied as carbon black or activated carbons. The activated carbons obtained from waste tyres have been tested successfully as adsorbents in the decolorisation of wastewater, in terms of methylene blue adsorption capacity⁵ and the removal of a variety of organic compounds and metals from aqueous solutions^{2,6}.

The preparation of activated carbons is the most studied alternative for the valorization of waste tyres char. In general, the chars obtained from pyrolysis of waste tyres show low surface area values, around 50-100 m²/g of BET surface area (S_{BET})^{2,7-9}. Hence, activation

by different methods, mainly using steam and CO₂, is needed¹. In this way it is possible to produce activated carbons with a wide range of pore volume and pore size distributions to be used in different applications. Helleur et al.² reported S_{BET} values of 240-275 m²/g after the activation with steam and carbon dioxide at temperatures around 900°C at burn-off values of 10-40%. Substantially higher values (200-1100 m²/g) have been reported by San Miguel et al.⁶ for the activation with steam and CO₂ at 925-1100 °C, but with burn-off levels up to 80 %. Literature shows as a general trend that to reach S_{BET} higher than 300-400 m²/g through physical activation it is necessary to operate at high burn-off implying low final yields.

Most of the works in literature are devoted to physical activation with steam and CO₂, whereas little attention has been paid to oxygen as activating agent. Oxygen exhibits a very high reactivity with chars and thus provokes a poor development of porosity, centered mostly in macropores and associated to high burn off values².

Py et al.¹⁰ reported an activation method based on oxygen chemisorption/desorption cycles to control the high reactivity of this activating agent. In this method, the first step of the cycle is chemisorption of oxygen at moderate temperatures using air or oxygen-containing mixtures. Afterwards, the chemisorpted oxygen is desorbed at high temperature in inert atmosphere. In these conditions the oxygen is desorbed as CO and CO₂ leaving new reactive carbon sites. This method is also reported as effective for pore size widening.

Activation by cyclic chemisorption/desorption requires the optimum temperature and time for each step of the cycle to be conveniently established. When the char is heated in the

presence of oxygen, chemisorption and desorption are competitive phenomena. At low temperatures chemisorption prevails, while desorption is the dominant process at high temperature. Desorption temperature is of importance since it influences not only the amount of carbon that is evolved as CO or CO₂, but also the type of oxygen-carbon associations that decompose giving rise to pore development.

In this work air has been used as activating agent for surface area development by cyclic chemisorption-desorption from a char obtained from pyrolysis of waste tyres. In a first approach the temperature and time for chemisorption and desorption steps are optimized. Then the development of porous structure is studied focused on surface area and pore volume.

MATERIALS AND METHODS

Experimental setup

The char was obtained from pyrolysis of waste tyres in a quartz vertical reactor placed inside of a sandwich-type electrical furnace. The reactor was 50 mm in diameter and 500 mm in length. Figure 1a shows the experimental set-up. A downward nitrogen flow was maintained through the reactor by means of a mass flow controller. A sample cup was held in the reactor by means of a rod introduced from the top. The rod permits to displace the cup with the rubber sample from the top of the reactor, where an inert atmosphere can be maintained due to the downward nitrogen flow, to the center of furnace where the reaction takes place. After the programmed reaction time, the cup is raised again to the top to be cooled by the incoming nitrogen flow. The gases produced upon pyrolysis are cooled, washed and evacuated.

The activation cycles were carried out in a quartz fixed bed reactor heated by an electrical furnace (Figure 1b). The bulb where the sample is placed is 20 mm x 50 mm. The gas flow was introduced by a mass flow controller through the bottom of the reactor after preheating in the lower part of the furnace. The sample was supported on a sintered porous quartz plate to avoid channelling. The temperature was controlled thanks to two thermocouples, one of them inserted in the bed and the other one placed close to the furnace wall. Waste gases were cooled, H₂O-scrubbed and evacuated.

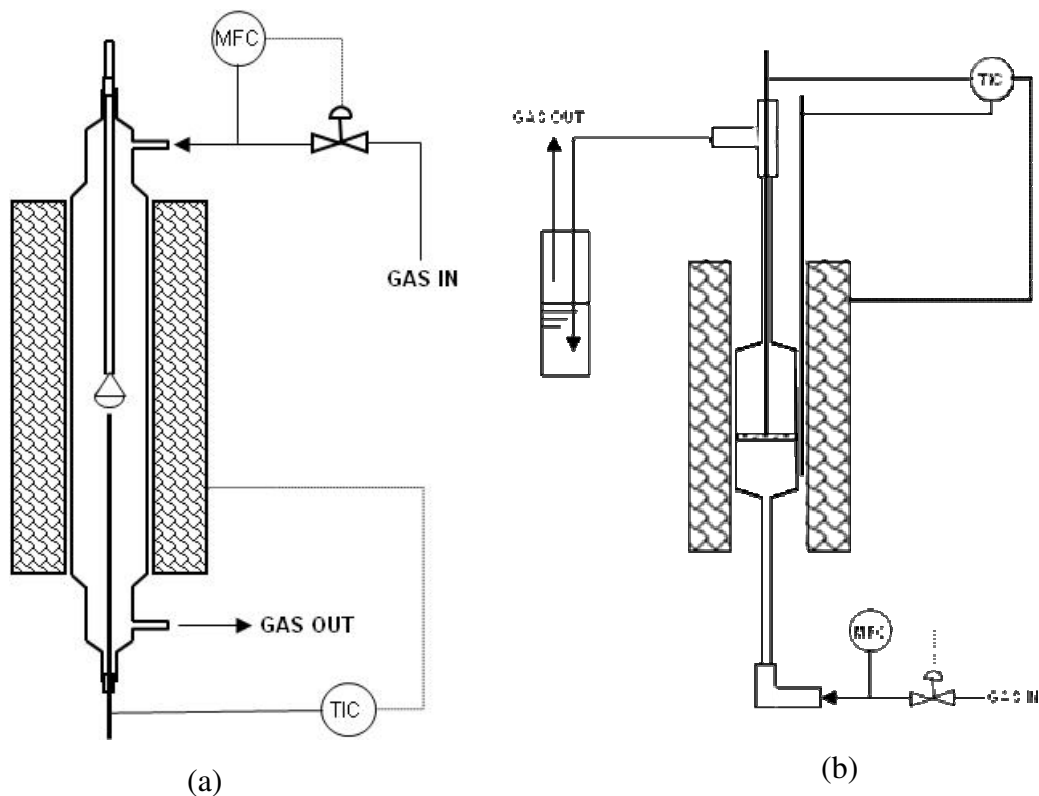


Figure 1. Experimental set-up for the pyrolysis (a) and activation (b) runs.

Preparation of char

Waste rubber was separated mechanically from the tread strip of Pirelli P2000 waste tyres. After cryogenic grinding in liquid nitrogen and sieving, a fraction of 1-2 mm particle size was selected as starting material to produce char. The char was obtained by isothermal fast pyrolysis at 800°C under 100 NmL/min of nitrogen flow and it was held at that temperature for 20 min. In each pyrolysis run, 1-2 g of waste tyres rubber was placed in the cup. These conditions were selected according to the results obtained in previous works focused on the

optimization of waste tyres carbonization¹¹. The yield was 41% and the elemental composition of the char obtained is showed in Table 1.

Table 1. Composition of waste tyre char (% weight basis)

C	H	N	S	OTHERS (*)
89.3	0.5	0.3	2.1	7.8

() Includes ash (Si, Zn, Ca and other minor elements) and oxygen*

Activation of char

In each experiment, 0.5 g of char was placed into the fixed bed reactor and heated under 100 NmL/min nitrogen flow up to 210°C; the heating rate up to this temperature was 15°C/min. Then the nitrogen flow was switched to an 80 NL/min air flow which was maintained during 3 hours to enable oxygen chemisorption. Afterwards, the flow was switched again to nitrogen and the sample was heated, using same heating rate, to the desired desorption temperature (550 or 750 °C) and maintained for 2 h. After completion of each cycle, the sample was weighted and its porous structure analysed.

Characterisation of samples

Oxygen chemisorption was studied by temperature programmed desorption (TPD) and thermogravimetric analysis (TGA). TPD was carried out by heating the sample up to 900°C in He flow at a heating rate of 10 °C/min and analysing the CO and CO₂ evolved with a non-dispersive infrared absorption analyser (Siemens Ultramat 22). The TGA system consisted of a quartz tube where a quartz sample pot was suspended from a CI Instruments

electronic head balance. The S_{BET} and the pore size distribution of the samples were determined from nitrogen adsorption-desorption at 77 K using a Quantachrome Autosorb I apparatus. The S_{BET} was calculated by a Multipoint method while the t-method was used to calculate the micropore volume and external or non-micropore area. Scanning electron microscopy (SEM) was performed in a Hitachi S-3000N device.

RESULTS AND DISCUSSION

TGA study of the oxygen chemisorption / desorption

In a first approach a series of chemisorption/desorption experiments were carried out to establish the most adequate temperatures for the activation cycles. Oxygen chemisorption and desorption rates are known to increase with temperature. Chemisorption can take place from temperatures as low as 200°C, whereas desorption can be already significant at such temperature¹². The maximum net uptake of oxygen for a number of carbonaceous materials has been found to take place between 200 and 350 °C¹⁰. Figure 2 shows the TGA curves corresponding to the chemisorption of oxygen by the char between 200 and 250 °C, where it can be observed an increase during the first three hours and beyond that time no significant change can be appreciated. The stabilization of the weight of the sample suggests a balance between sorption and desorption. Therefore, the chemisorption time was set to 3 hours. A weight increase of 0.32, 0.65, 0.41 and 0.23 % (initial weight basis) can be observed for the runs carried out at 200, 210, 230 and 250 °C, respectively. The increase in weight during the chemisorption is rather low (< 1%), therefore the burn-off expected in each cycle is also low. At 210°C the balance between chemisorption and desorption leads to

the maximum net weight gain, which is convenient in order to achieve a burn-off as high as possible in each activation cycle. This result is in agreement with a previous work by Py et al.¹⁰ that reported a temperature of 200°C as the most convenient to perform oxidation without combustion for several carbonaceous materials.

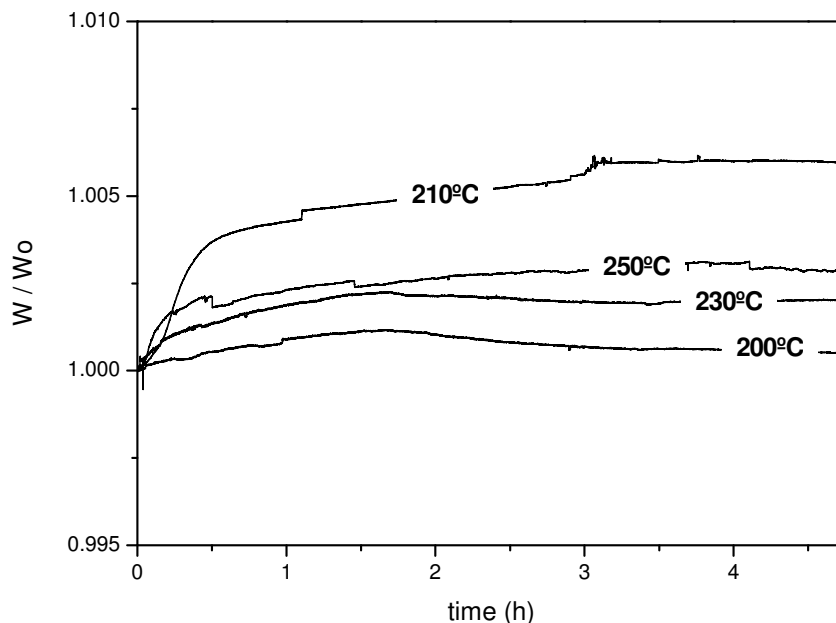


Figure 2. Relative mass variation upon oxygen chemisorption at constant temperature.

Attending to the TPD curves (Figure 3), the amount of CO₂ desorbed up to 850°C is similar in all the cases, except when the chemisorption experiment was carried out at 200°C, where the lower desorption of CO₂ is consequent with the lower uptake of oxygen observed. For chemisorption temperatures of 230 and 250 °C, the desorption pattern of CO₂ is similar, i.e., desorption becomes important beyond 300°C and becomes maximum around 550°C. In the case of chemisorption at 210°C, no significant desorption was observed up to 400°C, showing two CO₂ desorption peaks at 525 and 625 °C approximately; besides, a significantly higher amount of CO₂ was evolved beyond 700°C in this case. Based on the

TPD profiles, two desorption temperatures, 550 and 750°C, were selected for the study of the activation cycles. A heat treatment of the oxidized char at 550°C would provide the evolution of most of the first CO₂ peak, whereas at 750°C it would cover almost completely both the first and second peak. The amount of oxygen evolved as CO in TPD was found to be almost negligible below about 850°C.

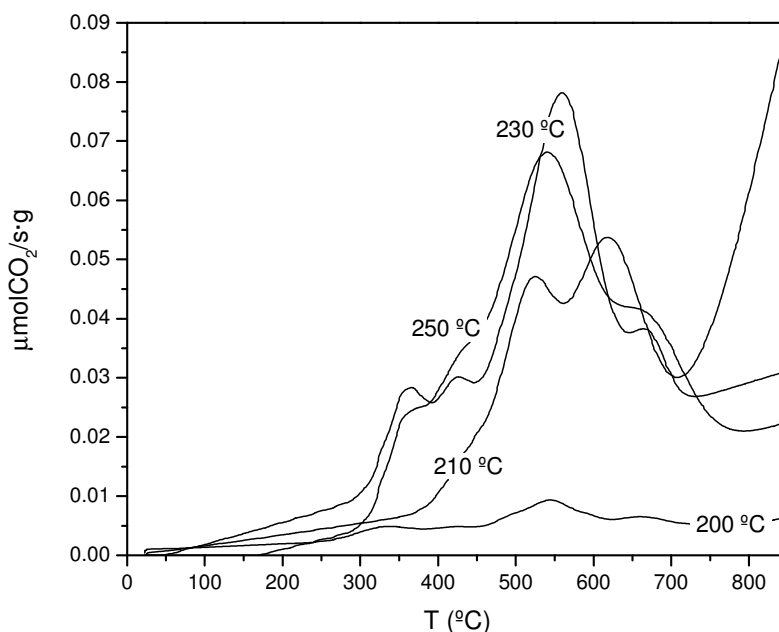


Figure 3. TPD curves of char after oxygen chemisorption.

Figure 4 shows the TGA curves in nitrogen atmosphere corresponding to desorption step at 550 °C and 750°C for a char oxidized at 210°C. Although desorption is much slower at 550 °C, at both temperatures most of the weight loss takes place within the first four hours. Thus, a 4-hours time was set for the desorption step.

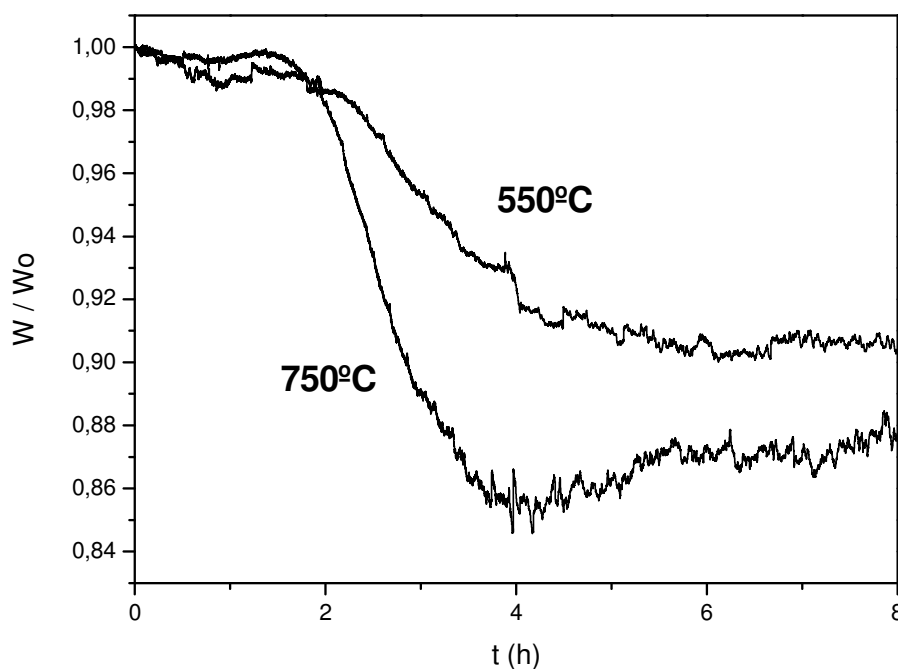


Figure 4. TGA desorption patterns at 550 and 750 °C.

Activation by cyclic oxygen chemisorption-desorption

Figure 5 shows the evolution of burn-off with the number of cycles for the set of experiments carried out at desorption temperatures of 550 and 750° C. In all cases the chemisorption step was carried out at 210 °C. As it can be seen, the burn-off shows a nearly linear dependence on the number of cycles applied to the char, excluding the first cycle which yields a higher burn-off. For the rest, a linear fit provided always values of r above 0.99. From the slope a variation of 1.09 and 1.41 points of percent burn-off per cycle can be deduced at 550 and 750° C desorption temperatures, respectively. Thus, the chemisorbed oxygen evolved as CO_2 at temperatures higher than 750° C in TPD (Figure 3) does not

seem to build up on the char surface blocking the reactive sites. Therefore, successive activation cycles do not affect significantly to the reactivity of the char.

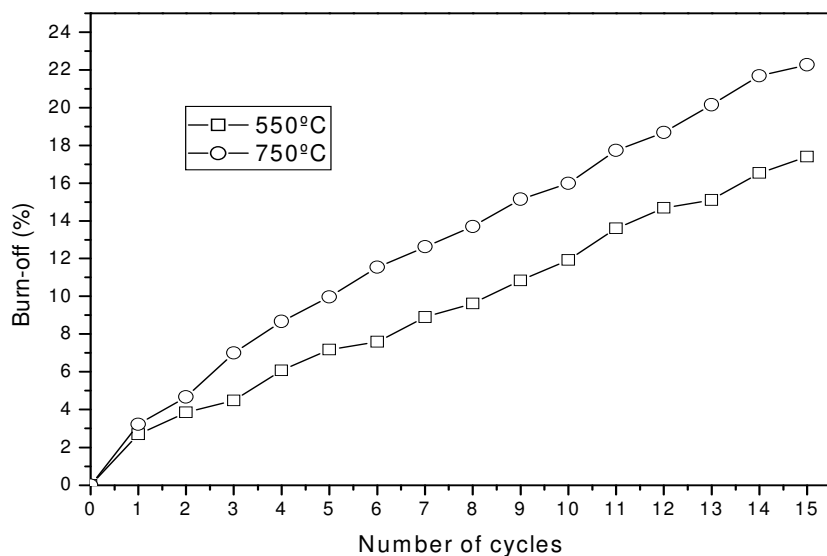


Figure 5. Burn-off evolution upon cyclic chemisorption-desorption.

The final burn-off values achieved after 15 activating cycles were 17.4 and 22.3 % for the samples treated at desorption temperatures of 550 and 750 °C, respectively. These burn-offs are equivalent to that reported by Py et al.¹⁰ for the activation of coal and pyrolyzed tar pitch by cyclic adsorption/desorption of oxygen from air flow.

Figure 6 shows the evolution of S_{BET} with the number of cycles applied. The highest increase is observed up to the fourth or fifth cycle and then a lower but monotonical increase is maintained. During the first three cycles the samples treated at 550 and 750 °C exhibit a fairly similar behaviour, but beyond that point the development of S_{BET} area is significantly

higher for the samples treated at 750°C desorption temperature, which is in accordance with the higher burn-off achieved. After 15 cycles, values of 156 and 239 m²/g were obtained at 550 and 750 °C, respectively. These results are rather low when compared with those reported by Mui et al.¹ for the activation of waste tyres char with steam and CO₂ (up to 1200 m²/g) although fairly different conditions were used leading to much higher burn-off values (up to 80%) and consequently substantially lower final yields. Helleur et al.² studied the preparation of activated carbons from steam and CO₂-gasification of waste tyres char reporting S_{BET} values between 200 and 300 m²/g at burn-off values of 13 to 38 %, whereas negligible S_{BET} values were obtained when using 2% O₂ at 725 – 750 °C up to 10-15% burn-off. At high temperature, the high reactivity of oxygen led to uncontrolled oxidative destruction of the char particles without significant development of porosity. This problem can be avoided through the cyclic oxygen chemisorption-desorption process tested in this work which provides a way of controlling the activation process.

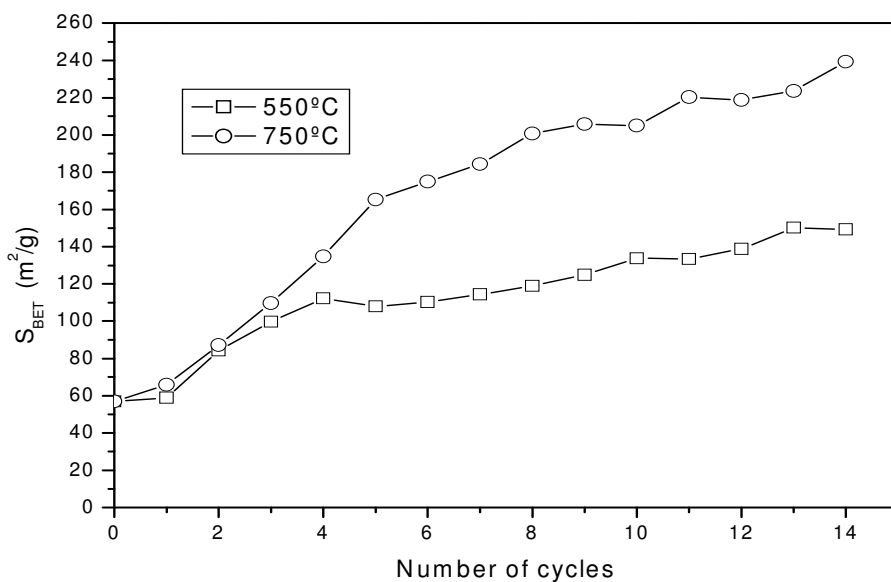


Figure 6. S_{BET} vs. cycle number for 550 and 750 °C desorption temperature.

Figure 7 shows the evolution of the micropore and narrow mesopore (2 - 8 nm) volumes with the number of cycles. In the first cycles the development of surface area is associated almost exclusively to mesoporosity for the two desorption temperatures tested. A maximum development of narrow mesoporosity is observed after the fifth cycle regardless the desorption temperature. Thus, a decrease of mesopore volume within this size range (2 – 8 nm) is noticed, most probably as a result of mesopore widening. The microporosity increases with the number of cycles applied and the values obtained after fifteen cycles are 0.035 and 0.060 cm³/g for a desorption temperature of 550 and 750 °C, respectively. These values are substantially lower than those reported by Py et al.¹⁰ for the activation of other materials by cyclic adsorption/desorption (0.2-0.6 cm³/g). These differences in surface area development can be due mostly to the starting materials used by Py et al., where the initial microporosity leads to a higher oxygen chemisorption enhancing pore development. The starting char is composed by the original carbon black, the carbon generated from rubber and some deposited pyrolytic carbon. Since these carbons may have different reactivity, the low increase observed in microporosity could be partly due to partial regeneration of the active surface associated to the type of carbon gasified preferentially in the first activation cycles, which deserves further study to understand pore development control.

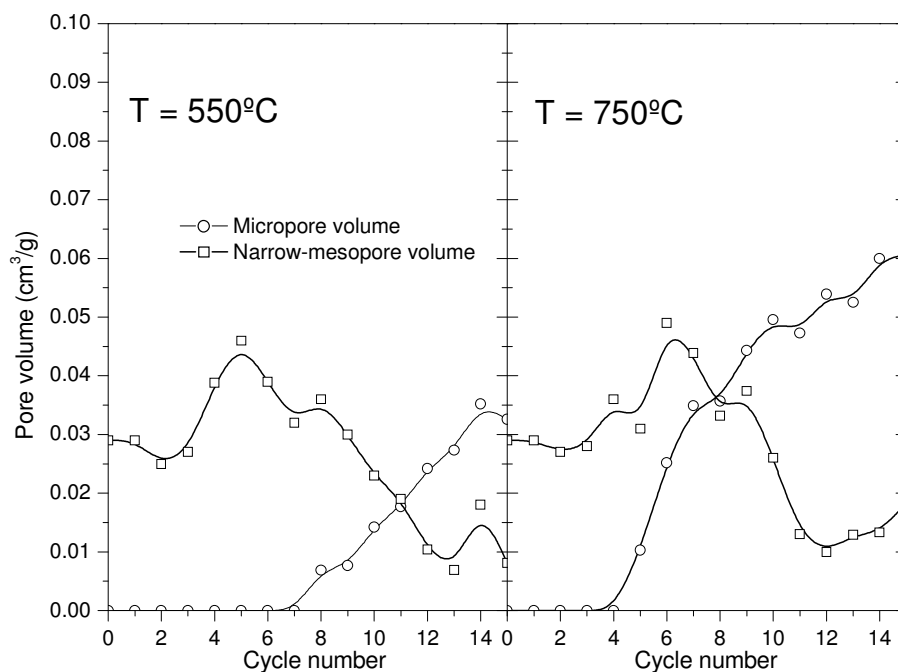


Figure 7. Micropore and narrow mesopore volumes vs. cycle number.

Figure 8 shows the evolution of the mean pore size with the number of cycles applied. The starting char is essentially mesoporous. As a result of chemisorption-desorption cycles a decrease up to mean pore sizes around 15 nm is observed. During the first three cycles the mean pore size decreases dramatically, which can be attributed to the generation of narrow mesopores, since micropores only were observed to develop effectively in later cycles. Beyond this point the mean pore size decreases monotonically for a desorption temperature of 750°C due to a development of microporosity. A 550°C desorption temperature the mean pore size is stabilized up to the sixth cycle and then decreases monotonically in successive cycles. The stabilization from the second to the sixth cycle could be explained as a balanced creation of micropores and widening of mesopores.

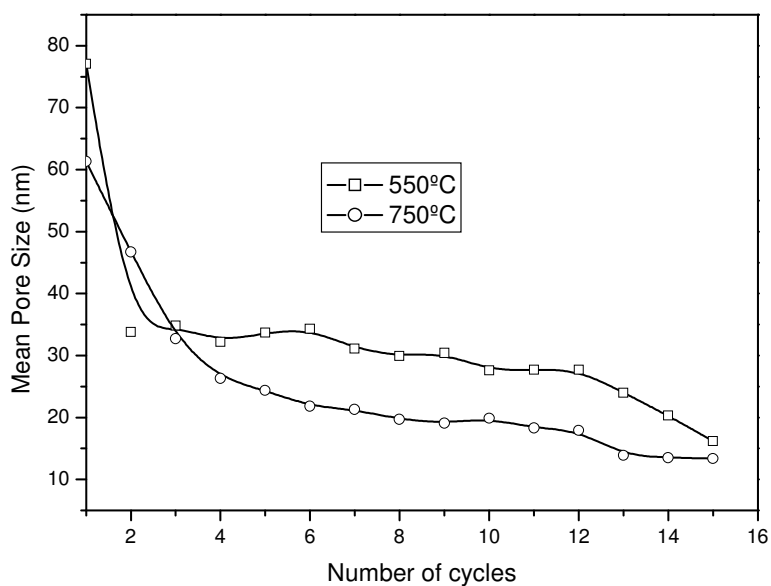


Figure 8. Evolution of the mean pore size with the number of cycles at 550 and 750 °C desorption temperatures.

Figure 9 shows the evolution of external or non-micropore surface area with the number of cycles applied at the two desorption temperatures tested. The evolution shows a fairly similar behaviour at both desorption temperatures consistently with the observed for the narrow mesopore volume. After an initial development of external surface a decline can be observed. Such decline takes place from the 4th cycle in the case of desorption at 550°C, and from the 9th cycle at 750°C. The maximum external surface area obtained is around 120 m²/g for the two desorption temperatures employed. This value is high in comparison with the results reported by Py et al.¹⁰ for other materials (5-70 m²/g).

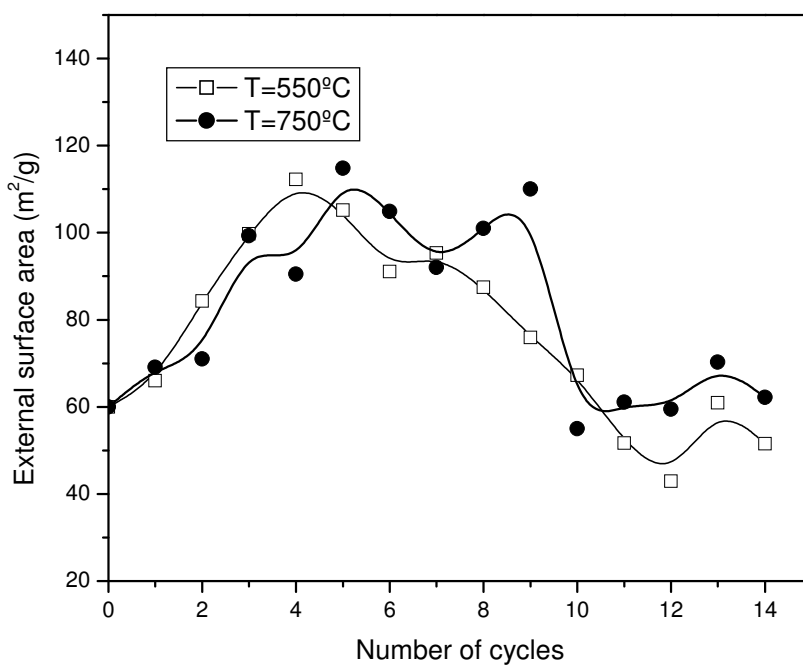


Figure 9. External surface area vs. cycle number

Although the development of porosity can be considered comparatively low, the external area achieved is above the average for most commercial activated carbons. This feature, in addition to the granular structure of the resulting activated carbons make them interesting candidates for some specific applications, such as catalysts supports particularly in liquid-phase processes. Thus, it is well known that mesopores allow an adequate dispersion of the metal on the support which results in a good catalytic activity¹³⁻¹⁵. Gurrath et al.¹⁶ reported advantages of mesoporous activated carbons as catalysts supports in liquid-phase cyclohexene and cyclooctene hydrogenation where steric but not diffusional effects could be influencing on the catalyst activity. Moreover, Calvo et al.¹⁷ found that mesopores were responsible for the good results obtained in 4-chlorophenol oxidation using activated carbon supported Pd catalysts.

Morphology

Figure 10 shows SEM images, at different magnification, of the samples obtained after 15 cycles at 550 and 750 °C desorption temperatures. The images indicate that the morphology of the particle is maintained after that high number of cycles. It can also be seen that the particle is formed by a continuous matrix where the carbon black and ash are embedded in the carbon generated from rubber by primary pyrolysis reactions and in pyrolytic carbon. This structure can provide a high mechanical strength than those based on agglomerated micrograins. That supports the potential interest of these activated carbons as catalytic supports for liquid-phase reactions. With this application in mind the optimum activation treatment consists in five chemisorptions-desorption cycles. A desorption temperature of 500°C is preferred since the development of external area is achieved with lower burn-off (7% in contrast to 10% at 750°C), which can contribute to a higher strength of the activated carbon granules.

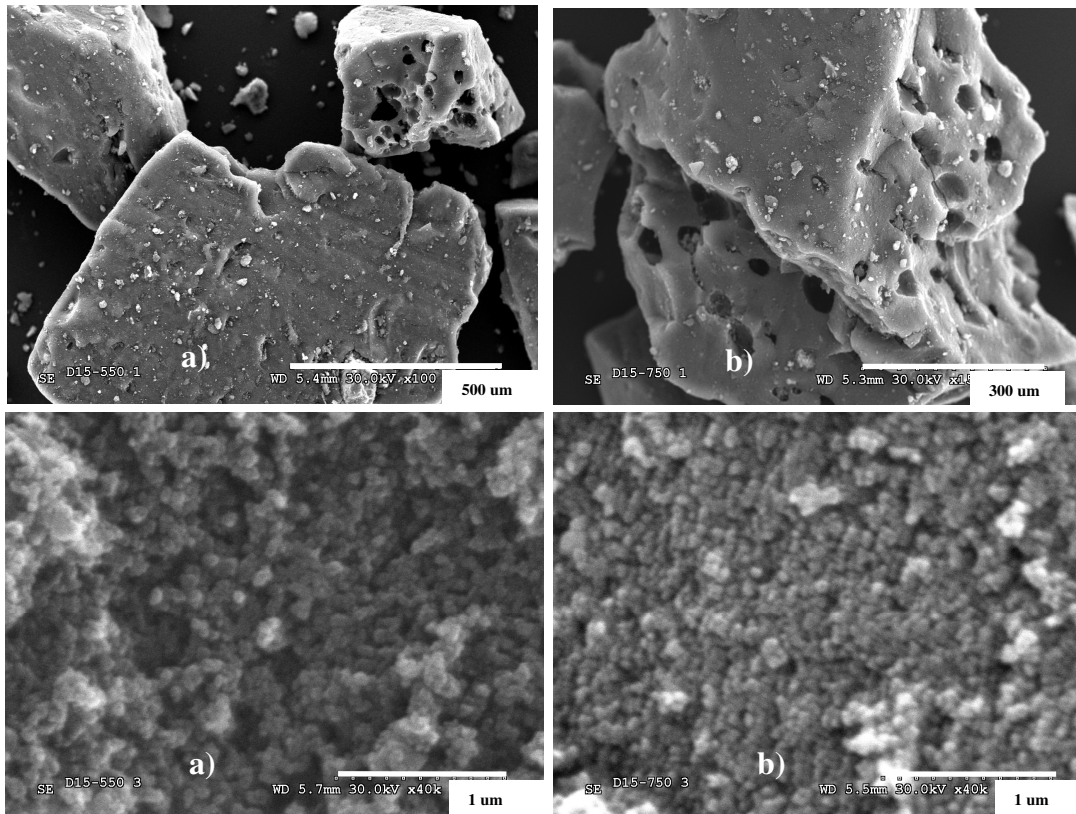


Figure 10. SEM images of the treated char after 15 cycles for a) 550°C and b) 750°C.

CONCLUSION

Cyclic adsorption-desorption of oxygen is revealed as a promising method for physical activation of waste tyres chars under controlled conditions. This method permits to control the high reactivity of oxygen, even at concentrations as high as those corresponding to air, to produce granular mesoporous activated carbons. With the method proposed it is possible to prepare activated carbons with BET surface area up to 220 m²/g at burn-off values lower than 20%, or with external and non-micropore area up to 120 m²/g at burn-off values as low as 6-9%. In the first activation cycles the porosity develops mostly by the generation of

narrow mesopores, and from cycles 4-6 the microporosity is developed. The different phases of porosity development could be the result of the gasification of carbon with different reactivity and capacity for the regeneration of active surface. As a result of the low burn-off values the particles morphology is maintained during activation and granular activated carbons are obtained. On the basis of this it can be postulated that the activated carbons prepared are interesting candidates for catalytic supports for liquid-phase applications.

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